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(54) Title: HYPERBRANCHED POLYESTER AND A PROCESS FOR ITS PREPARATION

(57) Abstract

The invention relates to a hyperbranched polymer comprising a nucleus and polyol and polycarboxy residues, the hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups and a Carothers gel point lower than 1. The hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups, is obtainable by starting with a nucleus compound containing at least one hydroxyl group as the nucleus and reacting it with a compound containing at least one anhydride group, after which the resulting first generation acid-terminated addition product is reacted with a compound containing at least one epoxy group; the resulting first generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second generation acid-terminated addition product, is reacted with a compound containing at least one epoxy group, resulting in a second generation hydroxyl-terminated addition product, and in at least one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.

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HYPERBRANCHED POLYESTER AND A PROCESS FOR ITS PREPARATION.

The invention relates to a hyperbranched polymer and a process for the preparation of a hyperbranched polymer.

Hyperbranched polymers are often referred to as "dendrimers" in the literature (see, for example, Encyclopedia of Polymer Science and Engineering, Index Volume, 1990, pp. 46-92).

Hyperbranched polymers (dendrimers) are three-dimensional, highly ordered oligomeric and polymeric molecules with a good defined chemical structure. These dendrimers differ from classical oligomers and polymers by their extraordinary symmetry, high branching and maximized terminal functionality density. They are formed from a functional core (nucleus) surrounded by a plurality of layers of branched structural units. The plurality of layers around the nucleus are called generations and in each generation the functionality of the macromolecule multiplies with the degree of branching of the structural units used. The resulting dendrimers have a tree-like structure (Greek: "dendrites") within ball-shaped macromolecules having a very high functionality and a very narrow molecular weight distribution. Such highly branched and highly functional macromolecules cannot be prepared by the conventional processes for making normal branched polymers because they would result in broad molecular weight distributions and in macroscopic gelling of the system.

In the article "One-step synthesis of hyperbranched dendritic polyesters" (J. Am. Soc. 1991, 113, 4583-4588), Hawker, Lee and Frechet describe hyperbranched polyesters.

Hawker et al. describe a synthesis of hyperbranched polyesters starting from dihydroxybenzoic acid which is

reacted with trimethylsilyl chloride and thionyl chloride to give di-trimethylsiloxybenzoyl chloride, after which the
5 hyperbranched polyester is formed by means of a one-step synthesis.

The Hawker process has many disadvantages. The process cannot be used on an industrial scale because of the reactants used, such as, for example, trimethylsilyl
10 chloride, thionyl chloride and benzoyl chloride, and because of the process stages such as the solvent process and the purification step. In particular, the large quantities of solvent which have to be distilled off make the process unattractive.

15 Another disadvantage of the Hawker process is the limited freedom of choice in the composition of the monomers to be used. This process consequently leads only to purely aromatic polyesters. However, in order to obtain a good balance in mechanical properties it must be possible to vary
20 the starting materials, such as aromatic and (cyclo)aliphatic monomers.

An object of the invention is to provide hyperbranched polymers. Another objective of the invention is to provide an industrially readily useable process for the
25 preparation of these hyperbranched polymers, which avoids the disadvantages and problems of conventional processes described above. A further objective of the invention is to provide a coating composition containing the hyperbranched polymers.

30 The hyperbranched polymer according to the invention is characterized in that it comprises a nucleus and polyol and polycarboxy residues the hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups and a Carothers gelpoint lower than 1.

35 Preferably the hyperbranched polymer has at least 8 terminal hydroxyl- or carboxyl groups; more preferably at least 10.

The gelpoint according to the Carothers equation, being the theoretical conversion factor at which the polymer 5 tends to gelate, preferably is lower than 0.95; more preferably lower than 0.90. The Carothers equation has been disclosed by G. Odian, Principles of polymerization, J. Wiley & Sons (1981), p. 113-116. Surprisingly, it has been found, that - although all the addition reactions almost 10 have a conversion factor of 1 - no gelation takes place.

The hyperbranched polymers according the invention have in general a relatively low polydispersity. The polydispersity of linear polyesters is about 2. Branched polyesters -made via direct and transesterification methods- 15 in general have very much higher polydispersities. In contrast, the polymers according the invention in general have a low polydispersity although it may steadily increase with (very) high branching. In case the nucleus has a polydispersity of 1, than the polydispersity of the polymer 20 can be depicted by the following formula:
 $D/[no.generations] < 2$. Preferably $D/[no.generations] < 1.8$. In case the nucleus has a polydispersity higher than 1, the figure has to be multiplied with the dispersity of the nucleus.

25 The hyperbranched polymer is obtainable by starting with a nucleus compound containing at least one hydroxyl group and reacting it with a compound containing at least one anhydride group, after which the resulting first-generation acid-terminated addition product is reacted 30 with a compound containing at least one epoxy group; the resulting first-generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second-generation acid-terminated 35 addition product is reacted with a compound containing at least one epoxy group, resulting in a second-generation hydroxyl-terminated addition product whereby in at least one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.

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Both the addition reactions are repeated alternatively in order to obtain a hyperbranched polymer of 5 the generation that is desired. Each generation step increases the molecular weight of the resulting hyperbranched polymer.

The reaction mechanisms in the subsequent generations are identical with those in the second 10 generation.

The abovementioned nucleus with hydroxyl groups is regarded for the sole purpose of definition as being of generation zero; the first acid-terminated and hydroxyl-terminated addition products are of generation one; 15 the second acid-terminated and hydroxyl-terminated addition products are of generation two, etc. Generally, the obtained hyperbranched polymer has 1-20 generations; preferably 2 or more generations and very preferably 3-10 generations.

The nucleus, which can be a monomeric, oligomeric 20 or polymeric compound, contains at least one hydroxyl group. Preferably, the nucleus contains 1-10 hydroxyl groups; more preferably this is 2-8.

If required, the nucleus can be formed by the addition reaction of a compound containing at least one 25 carboxyl group and a compound containing at least one epoxy group, resulting in a hydroxyl-terminated addition product.

Furthermore, a hydroxyl functional nucleus can be made -in case of oligomers or polymers- by well known esterification methods, urethane oligo- and polymerisation, 30 radical polymerisation and the like.

Mostly, the quantities of the added reactants are chosen in such a way, that substantially all terminal hydroxyl groups or acid groups of the nucleus or the respective addition products can react. Therefore, the 35 reactants are added in at least about an equimolar amount. Thus, the molar ratio between the terminal hydroxyl groups and the anhydride group containing compounds or between the terminal acid groups and the epoxy group containing compounds in all the reactions mentioned are about 1.1:0.9

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to 0.9:100; preferably 1.1:0.09 to 0.9:10; more preferably 1.1:0.9 to 0.9:1.1. Most preferably the molar ratios are 5 about 1:1, since at that moment extra purification steps are avoided.

The reaction temperatures can be chosen in a broad range. The reaction in all steps is usually carried out below 200°C, preferably below 180°C to avoid side reactions.

10 In order to obtain a good balance between reaction rates and reduction of side reactions, the reactions preferably are carried out at temperatures of between 80°C and 160°C.

Suitable compounds containing at least one hydroxyl group useful for being comprised in the nucleus are, for 15 example: glycols, for example 2,2,4-trimethyl-1,3-pentanediol, cyclo-hexane dimethanol, dipropyleneglycol, neopentyl glycol, 1,4-butanediol, 1,3-butanediol, 1,6-hexanediol or 1,8-octanediol; triols, for example glycerol, trimethylolethane and trimethylolpropane; polyols, for 20 example ditrimethylolpropane, pentaerythritol, di-pentaerythritol or sorbitol; and low molecular weight polyesters or polyurethanes having a molecular weight of, for example, about 3000. Other useful oligomers are e.g. polyethyleneglycol, polypropyleneglycol, monoalkylethers of 25 polyethylene- or polypropyleneglycol, and alkoxyLATED bisphenol-A, such as with 2-12 units ethoxylated or propoxylated bisphenol, and the corresponding hydrogenated compounds.

Preferably, low molecular weight polyols are used 30 as the compound containing hydroxyl groups.

Suitable compounds containing at least one epoxy group (useful in making the nucleus and in making the generations) are, for example: monoepoxides, for example: monocarboxylic acidglycidylester (Cardura E10^a; Shell), 35 ethylene oxide, propylene oxide or phenyl glycidyl ether; hydroxyepoxides such as the glycidylester of hydroxypivalic acid, of hydroxybutyric acid, or of hydroxystearic acid; diepoxides, for example diglycidylterephthalate, bisphenol

- A based epoxyresins; diglycidyl ethers, for example: 1,6-hexanediol diglycidyl ether; or triepoxides, for example:
- 5 trimethylolpropane triglycidyl ether,
triglycidylisocyanurate, trimethylolethane triglycidyl
ether, the polyglycidyl ether of castor oil. In case
polyepoxides are used in the addition reactions of the
generations building, it is preferred to have, after the
10 addition reaction, a reaction that opens the remaining epoxy
groups, e.g. a reaction with water.
Preferably, monoepoxides are used in the generation
building, more preferably, Cardura E10^R and/or propylene
oxide are used.
- 15 Suitable compounds containing at least one carboxyl
group are, for example, acid-terminated polyesters
polyethers or polyurethanes, dicarboxylic acids, for example
isophthalicacid, terephthalicacid, adipicacid and for
example trimelliticacid.
- 20 Suitable compounds containing at least one
anhydride group are, for example, trimelliticacidanhydride,
succinicacidanhydride, pyromelliticacidanhydride, maleic-
acidanhydride, succinicacidanhydride, phthalicacidanhydride,
tetrahydropthalicacidanhydride, hexahydropthalicacid-
25 anhydride, butanesuccinicacidanhydride, glutaricacid-
anhydride and itaconicacidanhydride. In case polyacid-
anhydrides are used in the addition reactions of the
generations building, it is preferred to have, after the
addition reaction, a reaction that opens the remaining
30 anhydride groups, e.g. a reaction with water.
Preferably, trimelliticacidanhydride is used as the
compound containing anhydride groups for the generation
building.
- Suitable solvents are, for example, toluene,
- 35 benzene, aceton, ethyleneglycolmonobutyletheracetate,
n-methylpyrrolidine, methylisobutylketone,
methylethylketone, xylene and propyleneglycolmonomethyl-
etheracetate. If required, a mixture of solvents can be

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used. Preferably, methylisobutylketone is used as the solvent.

5 Suitable catalysts in the preparation of the hyperbranched polymer are, for example, tertiary amines, phosphonium salts and metal tin compounds. Suitable tertiary amines are e.g. dimethylbenzylamine, dimethylaminopyridine and dimethylethanolamine. Suitable phosphonium salts are

10 e.g. trifenylethylphosphoniumbromide and trifenylmethylphosphoniumchloride. Suitable metal tin compounds are e.g. dibutyltinoxide, dibutyltinlaureate and dibutylhydroxytinchloride. If required the addition reactions can be carried out without adding a catalyst.

15 Of course, it is possible to have urethane groups built in via chain lengthening reactions, or by the use of oligourethanes with anhydride or epoxy functionality.

The process can be readily used industrially and has the further advantage that there is large freedom in the
20 choice of the monomeric composition for the hyperbranched polymer. The successive generations can be built up from the same monomeric building-blocks in each generation, but -if required- it is also possible to use various monomeric building-blocks in distinct successive generations. Using
25 this process has the advantage of a large freedom in choosing these building blocks. Thus it is possible, for example, to use only aromatic compounds, such as, for example, trimelliticacidanhydride and phenyl glycidyl ether in the first generations, and to use combinations of
30 aliphatic and aromatic compounds in the outermost generations, as a result of which a macromolecule with a hard core and a soft shell results. This principle can also be employed in reverse. This results in a hyperbranched polymer, such as, for example, a hyperbranched polyester,
35 having a core-shell structure.

The hyperbranched polyester as a rule has at least 6 branches, and hence, at least 6 functional groups. Preferably, the polymer has at least 10 branches or 10 functional groups. The initial functional groups are either

hydroxy or carboxy. These groups may be modified (if required, only partly) by methods known per se, as long as
5 the temperature applied during these reactions does not allow substantial transesterification. Hence, as a rule, the temperature should remain below 180°C. For instance, acid groups may be neutralised with amines, metal hydroxides, yielding a water dispersable hyperbranched polymer. Also the
10 acid groups can be reacted with a (large) excess of diepoxy as to make an epoxy functional hyperbranched polymer. A hydroxy-functional polymer may be modified e.g. with a (large) excess of di-isocyanate to make an isocyanate functional dendrimer. Such an isocyanate functional dendrimer
15 may e.g. be modified with hydroxyethyl(meth)acrylate to make UV curable coatings.

The advantage of the hyperbranched polyesters is that they have a very high molecular weight coupled with a very low viscosity. As a result, they are very suitable for
20 use in coating compositions in order to increase the solids contents.

The invention is explained in more detail with reference to the examples which follow, without, however, being restricted thereto.

25

ExamplesExamples I-IVPreparation of hyperbranched polyester30 Example I (1st generation)

In a 3-litre reaction flask having a mechanical stirrer and a thermometer, 67 grams of trimethylolpropane (0.5 mol), 288 grams of trimellitic anhydride (1.5 mol) and 410 grams of propylene glycol monomethyl ether acetate were
35 warmed to 150°C under a constant stream of nitrogen, after which the temperature was kept at 150°C for 30 minutes. After cooling to 120°C, 750 grams of monocarboxylic acid glycidylester (Cardura E10® from Shell) (3.0 mol) and

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0.1% by weight of triphenylethylphosphoniumbromide were added, with the temperature being kept below 155°C. After 5 the acid number had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

Viscosity according to the falling ball method: 5.5 dPa.s (65% solid in propylene glycol monomethyl ether acetate, 23°C). Carothers gel point (PC) = 0.833.

10

Example II (2nd generation)

In a 3-litre reaction flask having a mechanical stirrer and a thermometer, 557 grams of the product (0.184 mol of solid resin) obtained from generation 1 and 212 grams 15 of trimelliticacidanhydride (1.104 mol) were warmed to 150°C under a constant stream of nitrogen, after which the temperature was kept at 150°C for 30 minutes. After cooling to 120°C, 552 grams of monocarboxylicacidglycidylester (Cardura E10® from Shell) (2.208 mol) and 0.1% by weight of 20 triphenylethylphosphonium bromide were added, with the temperature being kept below 155°C. After the acid number had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

Viscosity according to the falling ball method: 11 25 dPa.s (65% solid in propyleneglycolmonomethyletheracetate, 23°C) (PC) = 0.847.

Example III (3rd generation)

In a 3-litre reaction flask having a mechanical 30 stirrer and a thermometer, 553 grams of the product (0.077 mol of solid resin) obtained in generation 2, 177 grams of trimelliticacidanhydride (0.924 mol) and 170 grams of propyleneglycolmonomethyletheracetate were warmed to 150°C under a constant stream of nitrogen, after which the 35 temperature was kept at 150°C for 30 minutes. After cooling to 120°C, 462 grams of monocarboxylicacidglycidylester (Cardura E10® from Shell) (1.848 mol) and 0.1% by weight of triphenylethylphosphoniumbromide were added, with the temperature being kept below 155°C. After the acid number

- 10 -

had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

5 Viscosity according to the falling ball method: 21.5 dPa.s (65% solid in propyleneglycolmonomethyl ether acetate, 23°C). (PC) = 0.854.

Example IV (4th generation)

10 In a 3-litre reaction flask having a mechanical stirrer and a thermometer, 621 grams of the product (0.035 mol of solid resin) obtained in generation 3, 161 grams of trimellitic acid anhydride (0.840 mol) and 122 grams of propyleneglycolmonomethyl ether acetate were warmed to 150°C
 15 under a constant stream of nitrogen, after which the temperature was kept at 150°C for 30 minutes. After cooling to 120°C, 420 grams of monocarboxylic acid glycidyl ester (Cardura E10® from Shell) (1.680 mol) and 0.1% by weight of triphenylethylphosphonium bromide were added, with the
 20 temperature being kept below 155°C. After the acid number had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

Viscosity according to the falling ball method: 44 dPa.s (65% solid in propyleneglycolmonomethyl ether acetate, 23°C).

The resin properties of the products obtained after the various synthesis steps are shown in Table I.

Table I

30

Example	I	II	III	IV
Generation	1	2	3	4
Mn (theoretical)	2210	6360	14670	31275
35 Acid number	2.9	1.2	0.9	1.1
Viscosity (65% solid in propylene glycol monomethyl ether acetate)	5.5	11	21.5	44

40

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The viscosity (in dPa.s) was determined (at 23°C) according to the falling ball method (Nouy-v.d. Lande).

5 The acid number (mg of KOH/gram of resin) was determined by titration with an ethanolic potassiumhydroxide solution. (PC) = 0.855.

Examples V-VIII

10 Preparation of hyperbranched polyester

Example V (1st generation)

In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 100 grams of 15 trimethylolpropane (0.75 mol), 432 grams of trimelliticacidanhydride (2.25 mol) and 345 grams of propyleneglycolmonomethyletheracetate were warmed to 140°C, after which the temperature was kept at 140°C for 30 minutes. After cooling to 120°C, 0.2% by weight of 20 dimethylbenzylamine was added, after which 274 grams of propylene oxide (4.5 mol + 5% by weight excess) were metered in, with the temperature being kept below 125°C. After the acid number had fallen to less than 4 mg of KOH/gram of resin, 34 grams of propyleneglycolmonomethyletheracetate 25 were added and the resin was cooled.

Viscosity according to the falling ball method: 11 dPa.s (65% solid in propyleneglycolmonomethyletheracetate, 23°C).

30 Example VI (2nd generation)

In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 436 grams of the product (0.28 mol of solid resin) obtained in generation 1, 323 grams of trimelliticacidanhydride (1.68 mol) and 208 35 grams of propyleneglycolmonomethyletheracetate were warmed to 130°C, after which the temperature was kept at 130°C for 30 minutes. After cooling to 120°C, 0.2% by weight of dimethylbenzylamine was added, after which 214 grams of propyleneoxide (3.36 mol + 10% excess) were metered in,

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with the temperature being kept below 125°C. After the acid number had fallen to below 4 mg of KOH/gram of resin, 40 5 grams of propyleneglycolmonomethyletheracetate were added and the resin was cooled.

Viscosity according to the falling ball method: 27 dPa.s (65% solid in propyleneglycolmonomethyletheracetate, 23°C).

10

Example VIII (3rd generation)

In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 548 grams of the product (0.13 mol of solid resin) obtained in generation 2, 15 300 grams of trimellitic acid anhydride (1.56 mol) and 193 grams of propyleneglycolmonomethyletheracetate were warmed to 135°C, after which the temperature was kept at 135°C for 30 minutes. After cooling to 120°C, 0.2% by weight of dimethylbenzylamine was added, after which 199 grams of 20 propyleneoxide (3.12 mol + 10% excess) were metered in, with the temperature being kept below 125°C. After the acid number had fallen to below 4 mg of KOH/gram of resin, 38 grams of propyleneglycolmonomethyletheracetate were added and the resin was cooled.

25 Viscosity according to the falling ball method: 59 dPa.s (65% solid in propyleneglycolmonomethyletheracetate, 23°C).

Example VIII (4th generation)

30 In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 549 grams of the product (0.057 mol of solid resin) obtained in generation 3, 263 grams of trimellitic acid anhydride (1.37 mol) and 142 grams of propyleneglycolmonomethyletheracetate were warmed 35 to 135°C, after which the temperature was kept at 135°C for 30 minutes. After cooling to 120°C, 0.2% by weight of dimethylbenzylamine was added, after which 175 grams of propyleneoxide (2.74 mol + 10% excess) were metered in, with the temperature being kept below 125°C. After the acid

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number had fallen to below 4 mg of KOH/gram of resin, 55 grams of propyleneglycolmonomethylmethyletheracetate were added 5 and the resin was cooled.

Viscosity according to the falling ball method: 104 dPa.s (65% solid in propyleneglycolmonomethylmethylether-acetate, 23°C).

The resin properties of the products obtained after 10 the various synthesis steps are shown in Table II.

Table II

Example	V	VI	VII	VII
15 Generation	1	2	3	4
Mn (theoretical)	1060	2910	6600	14000
Acid number	3.9	2.5	3.0	3.8
20 Viscosity (65% solid in propylene glycol monomethyl ether acetate)	11	27	59	104

25

The viscosity (in dPa.s) was determined, at 23°C, according to the falling ball method.

The acid number (mg of KOH/gram of resin) was determined by titration with an ethanolic potassiumhydroxide 30 solution.

Examples IX-XIV

Example IX (1st generation)

35 In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 225 grams of trimethylolpropane (1.68 mol) and 504 grams of succinicacidanhydride (5.04 mol) were warmed to 110°C in a nitrogen atmosphere. After a few minutes the temperature was raised to 150°C and kept at

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that temperature for 3 hours. After cooling, the acid-number of the obtained first generation product (A) was determined:
5 399 mg KOH/gram. The viscosity was 31 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn (theoretical) = 434.
Polydispersity: 1.2-1.3.

Example X (1st generation)

10 In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 214 grams of (A), 387 grams Cardura E10™ (1.52 mol) and 0.1 gram dimethylaminopyridine were warmed to 150°C in a nitrogen atmosphere. The temperature was kept at 150°C until the acid-number was
15 lower than 3 mg KOH/gram. After cooling, the hydroxy-number of the obtained first generation product (B) was determined: 132 mg KOH/gram. The acid-number was 0.7 mg KOH/gram. The viscosity was 11 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn (theoretical) = 1191. Polydispersity: 1.3-1.7.

20

Example XI (2nd generation)

In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 229 grams of (B), 103 grams of trimellitic acid anhydride (0.54 mol), 332 grams of
25 methylisobutylketone and 0.1 grams dimethylaminopyridine were warmed to 100°C in a nitrogen atmosphere and kept at that temperature for 5 hours. After cooling, the acid-number of the obtained second generation product (C) was determined: 189 mg KOH/gram. The viscosity was 43 mPa.s
30 (Emila, 50% in methylisobutylketone (MIBK), 23°C). Mn (theoretical) = 1775. Polydispersity 1.4-2.4.

Example XII (2nd generation)

In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 199 grams of (C), 90 grams Cardura E10™ (0.35 mol) and 0.1 gram dimethylaminopyridine were warmed to 150°C in a nitrogen atmosphere. The temperature was kept at 150°C during 2 hours, while the loss of MIBK was distilled off. At the moment the acid-number was

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lower than 3 mg KOH/gram the product (D) was cooled and the MIBK was added again. The hydroxy-number of the obtained 5 second generation product (D) was determined: 116 mg KOH/gram. The acid-number was 0.3 mg KOH/gram. The viscosity was 23 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn (theoretical) = 3245. Polydispersity 1.8-3.2.

10 Example XIII (3rd generation)

In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 176 grams of (D), 48.5 grams of trimellitic acid anhydride (0.25 mol), 117 grams of methylisobutylketone and 0.05 grams dimethylaminopyridine 15 were warmed to 100°C in a nitrogen atmosphere and kept at that temperature for 6 hours. After cooling, the acid-number of the obtained third generation product (E) was determined: 157 mg KOH/gram. The viscosity was 87 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn (theoretical) = 4397.

20 Polydispersity: 2.2-3.2.

Example XIV (3rd generation)

In a 1-litre glass reactor having a mechanical stirrer and a thermometer, 230 grams of (E), 101.6 grams 25 Cardura E10™ (0.40 mol) and 0.1 gram dimethylaminopyridine were warmed to 150°C in a nitrogen atmosphere. The temperature was kept at 150°C during 2 hours, while the loss of MIBK was distilled off. At the moment the acid-number was lower than 3 mg KOH/gram the product (F) was cooled and the 30 MIBK was added again. The hydroxy-number of the obtained third generation product (F) was determined: 112 mg KOH/gram. The acid-number was 0.6 mg KOH/gram. The viscosity was 62 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn (theoretical) = 7457. Polydispersity: 3.1

35

While the invention has been described in detail and with reference to specific embodiments thereof, it is apparent to one skilled in the art that various changes and modifications can be made therein without departing from the 40 spirit and scope thereof.

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Examples XV-XVIII

Preparation coating composition.

5 The products obtained in the Examples I, II, III and IV are used in the following coating compositions (respectively Examples XV to XVIII):

83.33 parts by weight of the product obtained

14.71 parts by weight hexamethoxymethylmelamine

10 1.96 parts by weight p-toluenesulfonicacid (Dynapol

Catalyst 1203, Hüls).

The obtained coating compositions were mixed with propyleneglycolmonomethyletheracetate until a solid content of 62% was reached. Next, a 100 µm film was made of these 15 polymer compositions using an Erichsen filmforming apparatus (type 360, width 60 mm) on a glass or steel surface. A curing cycle of 5 minutes at 200°C was used. The mechanical properties of the films obtained are given in the following table III:

20

Table III

Example coating composition	XV	XVI	XVII	XVIII
elasticity (mm)	5.5	7	8	8
reverse impact (inch/lb)	20	20	80	60
König hardness (sec)	63	137	123	106
acetone-resistivity (dR)	>100	>100	>100	>100

35

The elasticity is determined according to DIN 53156.

The reverse impact is determined according to ASTM-D-2794.

The König hardness is determined according to DIN 53157.

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Example XIX

A composition was made using:

- 5 27.01 parts by weight of the product obtained in Example III,
27.01 parts by weight Uralac XP 970 SH (solid resin, high molecular weight polyester, Mn 15000),
45.98 parts by weight propyleneglycolmonomethyletheracetate.

10 The viscosity of this polymer composition was 45 dPa.s (23°C, 54% solid).

Example XX

A composition was made using:

- 15 11.49 parts by weight of the product obtained in Example III,
34.48 parts by weight Uralac XP 970 SH (solid resin, high molecular weight polyester, Mn 15000),
54.02 parts by weight propyleneglycolmonomethyletheracetate.

20 The viscosity of this polymer composition was 11.5 dPa.s (23°C, 46% solid).

Examples XXI and XXII

The products obtained in the Examples XIX and XX
25 are used in the following coating compositions (respectively Examples XXI and XXII):

- 83.33 parts by weight of the product obtained
14.71 parts by weight hexamethoxymethylmelamine
1.96 parts by weight p-toluenesulfonicacid (Dynapol
30 Catalyst 1203, Hüls).

From the obtained coating compositions a 100 µm film was made of these polymer compositions using an Erichsen filmforming apparatus (type 360, width 60 mm) on a glass or steel surface. A curing cycle of 5 minutes at 200°C
35 was used. The mechanical properties of the films obtained are given in the following table IV:

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Table IV

5 Example XXI XXII
coating composition

	elasticity (mm)	8	8
10	reverse impact (inch/lb)	160	160
	König hardness (sec)	150	218
15	acetone-resistivity (dR)	40	40

The elasticity is determined according to DIN 53156.

The reverse impact is determined according to ASTM-D-2794.

20 The König hardness is determined according to DIN 53157.

C L A I M S

- 5 1. Hyperbranched polymer comprising a nucleus and polyol and polycarboxy residues, the hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups and a Carothers gelpoint lower than 1.
- 10 2. Hyperbranched polymer according to claim 1, characterized in that the hyperbranched polymer has at least 8 terminal hydroxyl- or carboxyl-groups.
3. Hyperbranched polymer according to claim 1, characterized in that the Patton-index is lower than 0.95.
- 15 4. Hyperbranched polymer having at least 6 terminal hydroxyl- or carboxylgroups obtainable by starting with a nucleus compound containing at least one hydroxyl group as the nucleus and reacting it with a compound containing at least one anhydride group, after which the resulting first generation acid-terminated addition product is reacted with a compound containing at least one epoxy group; the resulting first generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second generation acid-terminated addition product, is reacted with a compound containing at least one epoxy group, resulting in a second generation hydroxyl-terminated addition product, and in at least 20 one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.
- 25 5. Hyperbranched polymer according to claim 4, characterized in that the hyperbranched polymer has 1-20 generations.
- 30 6. Hyperbranched polymer according to one of claims 4-5, characterized in that the nucleus is formed by the addition reaction of a compound containing at least one carboxyl group and a compound containing at least one epoxy group.
- 35 40

- 20 -

7. Hyperbranched polymers according to one of claims 4-6, characterised in that the nucleus contains 1-10 hydroxyl groups.
- 5 8. Hyperbranched polymers according to one of claims 4-7, characterized in that the nucleus is a low molecular weight polyol.
- 10 9. Hyperbranched polymer according to one of claims 4-8, characterized in that the compound containing at least one anhydride group is trimellitic acid anhydride.
- 10 10. Hyperbranched polymer according to one of claims 4-9, characterized in that the compound containing at least one epoxy groups is a monoepoxide.
- 15 11. Process for the preparation of a hyperbranched polymer, characterised in that a nucleus compound containing at least one hydroxyl group is reacted with a compound containing at least one anhydride group, after which the resulting first generation acid-terminated addition product is reacted with a compound containing at least one epoxy group; the resulting first generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second generation acid-terminated addition product, is reacted with a compound containing at least one epoxy group, resulting in a second generation hydroxyl-terminated addition product, and in at least one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.
- 20 12. Process according to claim 11, characterised in that the molar ratio between the terminal hydroxyl groups and the anhydride groups containing compounds or between the terminal acid groups and the epoxy groups containing compounds is about 1.1:0.9 to 0.9:100.
- 25 13. Process according to one of claims 11-12, characterised in that the temperature during the various reactions is between 80°C and 160°C.

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14. Use of hyperbranched polymers according to one of claims 1-10 or use of hyperbranched polymers obtained according to one of claims 11-13 in coating compositions.
- 5 15. Polymer, process and use, substantially as described in the description and the examples.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 93/00051

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.C1.5 C 08 G 63/12 C 08 G 63/42 C 09 D 167/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1.5	C 08 G

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A, 3459733 (W.M. BYRD, Jr. et al.) 5 August 1969, see column 1, line 36 - column 3, line 37; examples 9,12-14 ---	1,2,4-8 ,10-13
X	GB,A, 934782 (STANDARD OIL CO.) 21 August 1963, see claims 1-3,8,9,14; example 1 ---	1,14
X	Chemical Abstracts, vol. 108, no. 20, 16 May 1988, (Columbus Ohio, US), see abstract no. 168606z, & JP,A,62207318 (ASAHI GLASS CO.) 11 September 1987, see registry no. 112408-92-1; abstract ---	1 -/-

⁶ Special categories of cited documents : 10⁷ "A" document defining the general state of the art which is not considered to be of particular relevance⁸ "E" earlier document but published on or after the international filing date⁹ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or other means¹¹ "P" document published prior to the international filing date but later than the priority date claimed¹² "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹³ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹⁴ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁵ "A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Mailing of this International Search Report

28-06-1993

05.08.93

International Searching Authority

Signature of Authorized Officer

EUROPEAN PATENT OFFICE

D.H. KRISCHE

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	H.F. MARK et al., "Encyclopedia of Polymer Science and Engineering", index volume, 1990, John Wiley & Sons, New York, US, page 46, D.A. TOMALIA et al.: "Dendritic polymers", see pages 60-61, 64-65 (cited in the application) ---	1,2,4- 13,15
Y	US,A,4659778 (R.C. WILLIAMS) 21 April 1987, see claims 7-15; examples A,I,K; column 10, line 13 - column 11, line 7	1,2,4- 13,15
Y		1,2,4- 15
Y	US,A,4568737 (D.A. TOMALIA et al.) 4 February 1986, see column 2, line 40 - column 3, line 32; column 8, line 49 - column 9, line 15 -----	1,2,4- 15

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

NL 9300051
SA 71616

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/07/93. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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